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# Synthesis and structure of an aminoethyl-functionalized cyclopentadienyl vanadium(i) dinitrogen complex†

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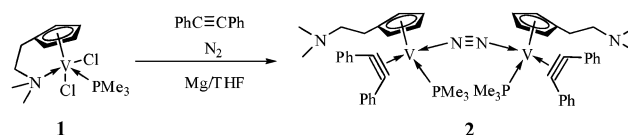
**Reduction of a V(III) complex  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{-VCl}_2(\text{PMe}_3)]$  in the presence of diphenylacetylene under nitrogen atmosphere yields a novel V(I) dinitrogen-bridged complex  $\{[\eta^5\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)]\text{V}(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)\}_2(\mu\text{-N}_2)$ .**

Transition metal dinitrogen complexes have received considerable attention due to the activation and functionalization of molecular dinitrogen,<sup>1</sup> which presents a unique opportunity to establish structure–reactivity relationships for nitrogen fixation and offer the possibility to discover new transformations. Although research on transition metal dinitrogen complexes have been documented with almost all metals,<sup>2</sup> so far, only a few reports on dinitrogen vanadium complexes are available.<sup>3</sup> Possible reasons are mainly due to the intrinsic properties of extremely air- and moisture-sensitive paramagnetic compounds and inherent instability associated with vanadium analogues. A cyclopentadienyl ligand with additional pendant Lewis basic functionality possesses remarkable versatility, such as chelate effect and hemilabile behavior. The chelate effect of pendant functionality can obviously enhance the stability of metal complexes, while the hemilabile behavior of pendant functionality can reversibly dissociate from the metal center. These features often lead to produce highly interesting new species.<sup>4</sup> We have been interested in the chemistry of vanadium complexes,<sup>5</sup> especially those of amino-functionalized cyclopentadienyl vanadium complexes.<sup>6–7</sup> Recently, we report a vanadium(III) complex  $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{VCl}_2(\text{PMe}_3)$ <sup>7a</sup> containing an amino-functionalized pendant chain, which it is a suitable starting material for the synthesis of a range of organometallic vanadium derivatives, not only of V(III) but also of V(II) and V(V).<sup>7b</sup> Thus, the discovery of thermally stable, isolable dinitrogen vanadium species do not only provide a unique opportunity to study dinitrogen coordination and to enrich the chemistry of vanadium complexes, but also explore the influence of ligand exchange between pendant amino functionality and dinitrogen on vanadium centers.

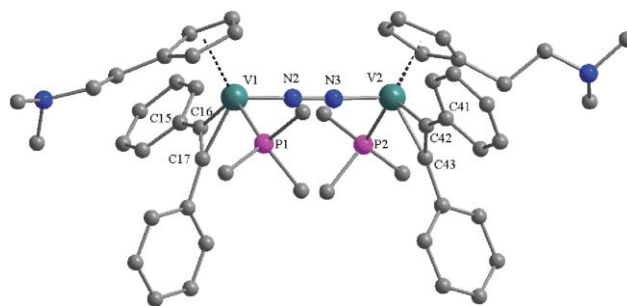
In this contribution, we present a novel aminoethyl-functionalized monocyclopentadienyl vanadium(i) dinitrogen complex  $\{[\eta^5\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)]\text{V}(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)\}_2(\mu\text{-N}_2)$  (**2**), which is synthesized *via* the reduction of  $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{VCl}_2(\text{PMe}_3)$  in the presence of

diphenylacetylene using an excess of magnesium as a reducing agent under N<sub>2</sub> atmosphere. Its molecular structure is determined and the pendant amino functionality to bind or to dissociate from the vanadium center is observed.

Aminoethyl-functionalized monocyclopentadienyl V(III) complex **1**, used as a synthetic precursor, was prepared according to the reported method.<sup>7a</sup> Two-electron reduction of the V(III) complex **1** with an excess of magnesium in THF afforded the red V(I) dinitrogen-bridged complex  $\{[\eta^5\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)]\text{V}(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)\}_2(\mu\text{-N}_2)$  (**2**, Scheme 1) in 31% isolated yield. Complex **2** is a diamagnetic, extremely air-sensitive red crystalline. The well-resolved NMR spectra, together with elemental analysis are consistent with its structure. The IR spectrum shows the useful information with coordinated PMe<sub>3</sub> (947.92, 1278.68, 1298.92 cm<sup>−1</sup>). Also the C–H vibration bands at 2760.83 and 2813.79 cm<sup>−1</sup> are consistent with the presence of non-coordinated NMe<sub>2</sub> groups.<sup>7,8</sup> The relatively high frequency of the  $\nu_{\text{C}\equiv\text{C}}$  vibration (1717 cm<sup>−1</sup>) indicates that the alkyne has less  $\pi$ -back-donation when compared to the alkyne with more  $\pi$ -back-donation in  $\text{CpV}(\text{PMe}_3)_2(\eta^2\text{-PhC}\equiv\text{CPh})$  ( $\nu_{\text{C}\equiv\text{C}}$  = 1600 cm<sup>−1</sup>).<sup>5b</sup> In addition, the high thermostability at room temperature suggests that **2** is more electronically favorable rather than sterically though extremely large steric hindrance around the vanadium center. Crystal structure determination (Fig. 1, selected bond lengths and angles in Table 1) shows that complex **2** has an idealized C<sub>2</sub> symmetry with the principal axis bisecting the N(2)–N(3) bond, in which two identical vanadium fragments  $[\eta^5\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{V}(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)]$  are linked by a



**Scheme 1** Preparation of the V(I) dinitrogen complex **2**.



**Fig. 1** Molecular structure of  $\{[\eta^5\text{-}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)]\text{V}(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)\}_2(\mu\text{-N}_2)$  (**2**): thermal ellipsoids are drawn at the 50% probability level.

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**Table 1** Selected bond lengths (Å) and angles (°) for **2**

V1–N2	1.761(6)	V2–C42	1.978(7)
V2–N3	1.773(6)	V2–C43	2.063(7)
N2–N3	1.212(8)	V1–N2	1.761(6)
V1–P1	2.385(2)	V2–N3	1.773(6)
V2–P2	2.373(3)	C16–C17	1.292(10)
V1–C16	1.996(7)	C42–C43	1.285(10)
V1–C17	2.059(7)		
V1–N2–N3	175.4(6)	P2–V2–C43	84.1(2)
V2–N3–N2	174.5(5)	N2–V1–C16	102.0(3)
P1–V1–C16	120.1(2)	N3–V2–C42	101.4(3)
P2–V2–C42	120.2(2)	C15–C16–C17	138.4(7)
P1–V1–C17	83.9(2)	C41–C42–C43	138.6(7)

bridging dinitrogen ligand. The coordination geometry can be best described as two lean square-pyramidal piano-stool configurations around two vanadium centers, in which each pendant amino functionality is not coordinated to the vanadium atom. The bridging dinitrogen ligand has a N(2)–N(3) bond distance of 1.212(8) Å, which is obviously elongated as compared to terminal N<sub>2</sub> ligands (1.111(17) Å<sup>2c</sup>). The V–N bond distances [1.761(6) and 1.773(6) Å] are obviously shorter than general V–N single bonds and slightly longer than general V=N double bonds. Overall these bond lengths in the core of the molecule confirm that the bridging dinitrogen are consistent with medium-activated dinitrogen ligand.<sup>1b</sup> These values are strongly similar to those of dinitrogen-bridged vanadium complex, where the N–N distance of 1.222(4) Å and the V–N distances of 1.770(3) Å are observed in {K(digly)<sub>3</sub>(μ-Mes)<sub>3</sub>V<sub>2</sub>(μ-N<sub>2</sub>)}.<sup>3a</sup> In addition, the alkyne's C(16)–C(17) and C(42)–C(43) distances of 1.292 (10) and 1.285(10) Å, together with the C–C–C(Ph) angles [C(15)–C(16)–C(17) = 138.4(7)° and C(41)–C(42)–C(43) = 138.6(7)°] of around 139° are consistent with an obviously lesser extent of π-back-donation in **2** than that in the V(I) complex CpV(PMe<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-PhC≡CPh),<sup>5b</sup> where the related parameters are 1.328(3) Å and 136°.

For comparison, the experiment under argon atmosphere was also carried out with similar reaction conditions. As a result, an extremely air-sensitive red crystalline was obtained in an acceptable yield. Attempts to get the crystals were unsuccessful. However, the well-resolved <sup>1</sup>H NMR and <sup>13</sup>C NMR indicated that this compound was also a diamagnetic compound. The C–H absorptions of 2760.83 and 2813.79 cm<sup>−1</sup> in the IR spectrum and the signals of PMe<sub>3</sub> protons in the <sup>1</sup>H NMR spectrum disappeared completely,<sup>7</sup> suggesting that this compound was a phosphine-free complex with the coordinated NMe<sub>2</sub> groups. Overall these characterizations speculated that this compound might be formulated as (η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)V(PhC≡CPh).<sup>7b</sup> In order to explore the reactivity of the V(I) dinitrogen-bridged complex, stirring **2** in THF solution at ambient temperature was carried out. A Toepler pump experiment showed only traces of nitrogen were pumped-off during several evacuation cycles in a high-vacuum line, suggesting the coordination of N<sub>2</sub> was quite robust. The equivalent of dinitrogen could be released quantitatively by the addition of a few drops of CH<sub>3</sub>OH *via* an NMR-tube experiment, in which the diphenylacetylene is produced at the same time.

In conclusion, the dimethylaminoethylcyclopentadienyl V(III) dichloride complex was a suitable organometallic vanadium starting material for development of a V(I) dinitrogen

complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)V(PhC≡CPh)(PMe<sub>3</sub>)<sub>2</sub>](μ-N<sub>2</sub>), which not only produces a new species and enriches organometallic vanadium chemistry, but can also offer an opportunity to compare its isostructural analogue. More importantly, it has been recognized that the pendant amino functionality can reversibly dissociate from the vanadium center.

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Characterization method: NMR spectra were recorded on Varian VXR-300 (300 MHz) spectrometers in NMR tubes sealed with a Teflon (Young) stopcock. IR spectra were recorded in a Mattson-4020 Galaxy FT-IR spectrometer from Nujol mulls between KBr disks unless stated otherwise. Elemental analyses were performed by Kolbe Analytical Laboratories, Mülheim a.d. Ruhr, Germany.

[(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)V(PhC≡CPh)(PMe<sub>3</sub>)<sub>2</sub>](μ-N<sub>2</sub>) (**2**): to 0.8 g activated Mg (33.3 mmol) was added a solution of (C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)VCl<sub>2</sub>(PMe<sub>3</sub>) (1.10 g, 3.29 mmol), together with PhC≡CPh (0.56 g, 3.13 mmol) in 20 mL of THF at −30 °C. The solution was allowed to warm to 0 °C and was stirred for another 30 min at this temperature. The solution changed from purple to deep-red. The solvent was removed *in vacuo* and the residue stripped with two portions of 5 mL of pentane. The dark-red solid was repeatedly extracted with 30 of pentane and 30 mL of ether. Concentrating to 5 mL and cooling the solution to −30 °C yielded 0.44 g (0.49 mmol, 31.1%) of red crystals. The suitable crystals for X-ray experiment were obtained by recrystallization in pentane. IR (Nujol Mull): 697.33, 720.48, 764.33, 793.36, 947.92, 1023.04, 1043.06, 1067.36, 1096.50, 1261.79, 1278.68, 1298.92, 1377.36, 1461.17, 1587.02, 1707.71, 2760.83, 2813.79, 2853.14, 2923.35, 2954.31, 3049.58, 3060.15 cm<sup>−1</sup>; <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 20 °C, 300 MHz): δ 7.80 (s, 2H, *Ph*), 7.23–6.60 (m, 8H, *Ph*), 5.71, 5.66 (d, 2H, *Cp*), 5.18, 5.14 (d, 2H, *Cp*), 2.63–2.47 (m, 4H, *CpCH<sub>2</sub>CH<sub>2</sub>N*), 2.21 (s, 6H, *NMe<sub>2</sub>*), 0.82, 0.79 (d, 9H, *J<sub>PH</sub>* = 7.5 Hz, *PMe<sub>3</sub>*); <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 20 °C, 75.4 MHz): δ 16.91, 17.15 (q, *J<sub>PC</sub>* = 72.9 Hz, *PMe<sub>3</sub>*), 28.96 (t, *CpCH<sub>2</sub>*), 45.71 (q, *NMe<sub>2</sub>*), 61.57 (t, *NCH<sub>2</sub>*), 97.66, 99.44, 101.06, 101.95, (all s, *C≡C*), 117.97, 123.88, 124.52, 125.98, 126.14, 126.71, 130.27, 139.32, 149.12, 151.15, 164.33, 176.96 (all d, *Ph C*); Anal. Calcd for C<sub>52</sub>H<sub>66</sub>N<sub>4</sub>P<sub>2</sub>V<sub>2</sub>: C, 68.56; H, 7.30; N, 6.15. Found: C, 68.54; H, 7.36; N, 5.98.

Crystal data: formula C<sub>52</sub>H<sub>66</sub>N<sub>4</sub>P<sub>2</sub>V<sub>2</sub>, *M<sub>r</sub>* = 910.95 g mol<sup>−1</sup>, triclinic, *P* $\bar{1}$ , *a* = 12.182(2) Å, *b* = 14.323(3) Å, *c* = 14.344(3) Å, α = 79.989(3)°, β = 83.952(3)°, γ = 88.051(3)°, *V* = 2450.6(8) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.234 g cm<sup>−3</sup>, *F*(000) = 964, μ = 4.85 cm<sup>−1</sup>, θ(max) = 24.11°. A red colored needle-shaped crystal with dimensions of 0.30 × 0.065 × 0.035 mm was mounted on top of a glass fiber, by using inert-atmosphere handling techniques, and aligned on a Bruker SMART APEX CCD diffractometer (Platform with full three-circle goniometer). The diffractometer was equipped with a 4 K CCD detector set 60.0 mm from the crystal. The crystal was cooled to 100(1) K using the Bruker KRYOFLEX low-temperature device. Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). SMART was used for preliminary determination of the unit cell constants and data collection control. Data integration and global cell refinement was performed with the program SAINT. The final unit cell was obtained from the

xyz centroids of 2436 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*<sup>9</sup>), and reduced to  $F_o^2$ . The program suite *SHELXTL*<sup>10</sup> was used for space group determination (*XPREF*). The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDF*.<sup>11</sup> The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Some atoms showed unrealistic displacement parameters when allowed to vary anisotropically, suggesting dynamic disorder (dynamic means that the smeared electron density is due to fluctuations of the atomic positions within each unit cell). Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Final refinement on  $F^2$  carried out by full-matrix least-squares techniques converged at  $wR(F^2) = 0.1761$  for 7680 reflections and  $R(F) = 0.0776$  for 3226 reflections with  $F_o \geq 4.0\sigma(F_o)$  and 551 parameters and 360 restraints. The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on  $F^2$  with full-matrix least-squares procedures minimizing the function  $Q = \sum_h [w(|F_o|^2 - k(F_c)^2)|^2]$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ ,  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes, respectively; ultimately the suggested  $a (= 0.0593)$  and  $b (= 0.0)$  were used in the final refinement.

Reduction of **1** in the presence of diphenylacetylene under argon atmosphere with the similar reaction condition. Red solid, yield: 54.6%; IR (Nujol Mull): 698.30, 726.21, 800.59, 1026.43, 1041.96, 1074.63, 1094.90, 1261.07, 1376.96, 1460.98, 1483.40, 1588.21, 2854.59, 2923.71, 2953.59  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 20 °C, 300 MHz)  $\delta$  6.89, 6.86 (d, 4H, *Ph*), 6.71 (t, 2H, *Ph*), 6.55 (t, 2H, *Ph*), 6.19 (s, 2H, *Ph*), 6.02, 6.04 (d, 2H, *Cp*), 5.73, 5.71 (d, 2H, *Cp*), 3.05 (t, 2 H,  $J = 6.9$  Hz,  $\text{CH}_2\text{Cp}$ ), 2.67 (t, 2 H,  $J = 6.9$  Hz,  $\text{CH}_2\text{N}$ ), 2.22 (s, 6 H,  $\text{NMe}_2$ ); <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 20 °C, 75.4 MHz):  $\delta$  28.64 (t,  $\text{CpCH}_2$ ), 45.65 (q,  $\text{NMe}_2$ ), 60.17 (t,  $\text{NCH}_2$ ), 105.86, 106.35 (all s,  $\text{C}\equiv\text{C}$ ), 124.07, 126.11, 126.74, 126.92, 127.25, 131.56, 142.31, 158.67 (all d, *Ph*, *Cp*,  $\text{C}=\text{C}$ ); Anal. Calcd for  $\text{C}_{23}\text{H}_{24}\text{NV}$ : C, 75.60; H, 6.62; N, 3.83. Found: C, 75.38; H, 6.65; N, 3.45.

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